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PATENT SPECIFICATION

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(72) Inventors:
 Geoffrey Arthur Byrne
 Ross Ian Aylott

(54) AN ACCUMULATOR FOR ORGANIC MATERIALS



(71) We, INVERESK RESEARCH INTERNATIONAL, a British Company of Inveresk Gate, Musselburgh, Midlothian, Scotland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to a device for accumulating organic materials from water systems. In particular, the device can be used to monitor the concentrations or variations in concentration of organic pollutants which are potentially toxic or harmful to aquatic and 15 human life and which are derived from effluent discharged into rivers, estuaries and seas, or derived from other sources by removing and analysing samples from said device.

20 There is worldwide concern over environmental pollution by organic pollutants which may be discharged into rivers, estuaries, seas and inland waterways. Although these compounds may be present in small quantities, 25 it is known that certain types of these compounds accumulate in aquatic plants and fish. Concern has been expressed about many organic compounds, for example, chlorinated materials such as dieldrin, aldrin and benzene hexachloride.

30 It is desirable to know whether there is an accumulation of such compounds over an extended period of time and to what extent any accumulation can be related to factors 35 such as effluent composition, tidal behaviour, and river flow. It is also desirable to establish a relationship between the accumulated total of a compound collected at any point over a known period of time and the average concentration in water passing that point

during that period. An aid to the identification and quantification of organic compounds present in very low concentrations in aqueous streams (information not easily obtained by conventional analysis of 'grab' samples) is

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Accordingly the present invention provides a device for accumulating organic materials from a water system, the device comprising a housing provided with an opening, a porous membrane adapted to act as a selectively permeable aqueous medium — organic medium interface, means for securing said membrane to said housing at said opening to constitute a selectively permeable barrier at said opening, an organic medium as herein defined within said housing filling said housing to a level at which said organic medium wets said membrane and said organic medium being capable of dissolving at least one type of organic molecule 60 diffusing through said membrane from an aqueous medium in contact with the outside of said membrane.

65 By the term "organic medium" is meant an organic liquid, an oil-in water emulsion, or a hydrophobic gel, each of which may optionally contain one or more complexing agents for the organic materials to be accumulated.

70 It is preferred for the organic medium (or herein defined) to be an organic liquid. Suitable organic liquids are benzene, xylene, toluene, hydrocarbons such as hexane and chlorinated hydrocarbons such as chloroform and carbon tetrachloride. However, other organic liquids possessing low solubility in water may be used.

75 With regard to the porous membrane of the device of the present invention, it is preferred that it be composed of a material selected from regenerated cellulose, vinyl chloride homo-

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polymers and copolymers, polyvinylidene fluoride, acrylonitrilepolyvinylchloride and polytetrafluoroethylene.	water.
For optimum operation it is preferred that	The laboratory work and the field trials together with the conclusions reached are now discussed.
5 the device should not be adversely affected by changes in, for example, pH temperature, solids content and biological and chemical oxygen demand of the water.	We refer first to the laboratory tests, and in particular to the experimental conditions. The present invention is also further illustrated in the following description with reference to the accompanying drawings, in which:—
10 The device is advantageously constructed to withstand variations in underwater currents and able to operate under a range of hydrostatic pressures. In general, the membrane has to be sufficiently robust to withstand knocks from fast moving solid objects in the water. Also,	Figure 1 is a diagrammatic elevation of a device of the present invention having a glass container with a vertical membrane; 70
15 the membrane should preferably not biodegrade during its working life.	Figure 2 is an axial section of a glass accumulator device of the present invention; 75
20 The device is generally designed so that the organic materials from the water under test can diffuse through the membrane at sufficiently high rates to allow accumulation of significant quantities of organic materials within a relatively short time. However, the organic medium should desirably not become saturated with dissolved organic compounds	Figure 3 is a sectional elevation of the device shown in Figure 2, in position on a river bed; 80
25 during the working life of the device which acts as an organic compound accumulator.	Figure 4 shows the location of the aqueous/ organic liquid interface in a pore of a hydrophilic membrane and also a hydrophobic membrane; 85
30 In general the organic liquid medium is chosen so that the concentrations of the accumulated organic compounds are not significantly reduced by back-diffusion through the membrane. Similarly, significant losses of the organic liquid medium from the device should not occur.	Figure 5 is a graph showing the results of the accumulation of 2-bromopropane by carbon tetrachloride; 90
35 The device is capable of selectively accumulating organic compounds of a particular type, i.e. of a particular solubility. It should not be swamped by organic compounds of no interest which may be present in considerably larger quantities than those organic compounds	Figure 6 is a graph showing the accumulation of dieldrin and γ -benzene hexachloride by hexane; 95
40 which are of interest. The trapped organic compounds should be readily processable for analysis once removed from the environment under test.	Figure 7 shows gas chromatograms of a hexane sample taken from an accumulator of the present invention and of a 'grab' sample extract of the water in which the accumulator had been immersed;
45 A preferred system comprises an accumulator device having a glass housing provided with an opening fitted with a regenerated cellulose membrane (Cuprothane [Registered Trade Mark], ex J.P. Bemberg; dry thickness — 10 μ m; pore size — 0.003 μ m;	Figure 8 shows a partly sectioned elevation of a device of the present invention incorporating a stirrer close to the membrane surface thereof; 100
50 water wet thickness — 20 μ m Approx. Pore Area % of total membrane area — 80) and filled with hexane. Hexane is the preferred organic solvent because it readily dissolves compounds of low water solubility, such as	Figure 9 is a detailed sectional elevation of the housing of the device shown in Figure 8; and
55 dieldrin, aldrin and benzene hexachloride which we are particularly interested in monitoring, it has very low solubility in water (significant losses of solvent from the accumulator do not occur in practice) and it is	Figure 10 is a side view of the motor and battery of the motor block of the device of Figure 8. 105
60 effective in preventing biodegradation of the cellulose membrane (this effect occurs at the water — membrane — solvent interface; in the absence of hexane (or carbon tetrachloride, toluene, benzene or other solvents) the cellulose membrane is biodegraded in river	1. <i>Apparatus</i>
65	The apparatus used for laboratory studies is shown in Figure 1 of the accompanying drawings. Figure 1 is a diagrammatic elevation of a glass container with a vertical membrane. 110
	A <u>polymer membrane</u> 1 in sheet form is located between the ground glass flanges 2 and 3 of two glass reaction vessels 4 and 5 respectively. Each flask is fitted with a side arm 6 and 7 for filling, stirring (when required) and sampling purposes. Although gaskets were used for initial laboratory studies it was later shown that their presence was not essential and that solvent leakage did not occur in their absence. The two flasks are held together by spring clips 8. Although chlorinated hydrocarbons have a slight softening effect on polyethylene at room temperature, no adverse effects were noted with carbon tetrachloride; if necessary PTFE gaskets, which are completely unaffected by chlorinated hydrocarbons, could be used instead. Vessel 4 contained an aqueous 115
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5	solution of an organic compound under test (e.g. dieldrin) and vessel 5 the organic solution (e.g. hexane).	The design of glass accumulators adopted for field work was shown in Figures 2 and 3 of the accompanying drawings.
5	This system was entirely satisfactory for experiments with Cellophane membranes (The word "Cellophane" is a Registered Trade Mark).	70
10	The membrane was desired to have the following properties:	
10	i) <u>High permeability towards organic molecules</u> : since transport rate is inversely proportional to membrane thickness, very thin membranes were desirable	75
15	ii) <u>High mechanical strength and flexibility</u> : a balance was necessary between high strength and low membrane thickness	80
15	iii) <u>Chemical resistance and non-biodegradability</u> : in particular resistance to organic solvents such as hexane and carbon tetrachloride was needed	85
20	iv) <u>Consistent transport behaviour</u> : i.e. resistance to fouling.	90
25	In principle, any polymeric membrane material demonstrating these properties may be used. The usefulness of membranes which are swollen by the organic solvent will depend upon the degree of swelling and whether prolonged swelling results in slow dissolution or mechanical breakdown of the membrane.	
30	Thus, for example, the so-called Gelman (the word "Gelman" is a Registered trade mark) filters in Table I may be used for those solvents with the code G (e.g. triacetate membrane may be used with an accumulator containing carbon tetrachloride but not with one containing chloroform).	95
35	Although hydrophobic membranes such as polypropylene can be made to work, we prefer hydrophilic membranes.	100
40	2 Assembly of glass accumulators for laboratory studies	105
45	The Cuprophane membranes contained about 17% glycerol as plasticiser. Before assembly, the glycerol was removed by soaking the membrane in distilled water for 30 minutes and then replacing the water by two successive portions of distilled water. The wet membrane was then fitted across the face of the accumulator as shown, still in the wet condition. Both compartments of the accumulator were then filled. Any small amount of water remaining on the surface of the 'trapping side' of the membrane became detached during filling and floated to the top of the organic liquid from where it was easily removed with a pipette. This effect occurred very infrequently.	110
50	In stirred systems, the stirrer (of the double link glass variety) was located centrally in the relevant compartment.	115
55	Temperature control is effected by locating the accumulator in a constant temperature ($\pm 0.5^\circ\text{C}$) water bath.	120
60	3 Assembly of glass accumulators for field trials	125
65	3 Assembly of glass accumulators for field trials	130

TABLE I.
CHEMICAL COMPATIBILITY OF GELMAN FILTERS

Chemical	Filter	Triacetate Metric ^c Type CA, Type P.E.M. Coloured Metric	Vinyl Metric ^c	Fluoride Metric ^c , Type VF	Alpha Metric ^c	Acropor ^a , Type AN	Acropor ^a , Type WR	Epoxy Versapor	Polypropylene
ALCOHOL									
Methanol	F G	G G	G G	G G	G G	G G	G G	G G	G G
Ethanol	G G	G G	G G	G G	G G	G G	G G	G G	G G
Isopropanol	G G	G G	G G	G G	G G	G G	G G	G G	G G
Propanol	G G	G G	G G	G G	G G	G G	G G	G G	G G
Butanol	G G	G G	G G	G G	G G	G G	G G	G G	G G
Amyl									
Tetrahydrofurfuryl									
ESTERS	D	P P	P P	F G G	G G G G G	P G G G G	F G G G G	P F G G	G G
Methyl Acetate									
Ethyl Acetate									
Isopropyl Acetate									
Butyl Acetate									
Amyl Acetate									
Cellosolve Acetate									
KETONES									
Acetone	P	P	P	P	G	P	P	P	G
Methyl Ethyl Ketone	D	P	P	F	G	P	F	F	G
Methyl Isobutyl Ketone	P	P	P	G	P	F	F	P	G
Cyclohexanone	D	D	D	P	G	P	P	P	G

TABLE I CONTINUED

Chemical	Filter	Tracetate Metrical Type GA, Type P.E.M. Coloured Metrical	Vinyl Type P.E.M. Coloured Metrical	Fluoride Metrical, Type VF	Alpha Metrical	Acropor, Type AN	Acropor Type WR	Epoxy Versapor	Polypropylene
GLYCOLS		G G G	G G G	G G G	G G G	G G G	G G G	G G G	G G G
Ethylene Propylene Glycerine									
GLYCOL ETHERS									
Methyl Cellosolve*	P	F	F	G	G	G	G	G	G
Butyl Cellosolve*	F								
ETHERS (MISC.)									
Diethyl Petroleum Diisopropyl Ether Tetrahydrofuran Dioxane	G G D D	G G P P	G G P P	G G G G	G G P P	G G P P	G G P P	G G G G	G G G G
HALOGENATED HYDROCARBONS									
Chloroform Methylene Chloride Carbon Tetrachloride Trichlorethylene	D D G G	P D G F	G G G G	G G G G	F P G G	G G G G	G G G G	G G G G	G G G G

TABLE I CONTINUED

Chemical	Filter	Triacetate Metricel Type GA, Type P.E.M. Coloured Metricel	Vinyl Metricel	Fluoride Metricel, Type VF	Alpha Metricel	Acropor. Type AN	Acropor, Type WR	Epoxy Versapor	Polypropylene
HALOGENATED HYDROCARBONS (Contd)									
Freon **TF	C	G	G	G	G	G	G	G	G
Perchloroethylene	C	G	G	G	G	G	G	G	G
Chlorothene ***NU	C	F	G	G	G	G	G	G	G
Gensolv + D		F	G	G	G	G	G	G	G
Dowclene ***WR	C								
AROMATIC HYDROCARBONS									
Benzene	C	P	G	G	G	G	G	G	G
Toluene	G	P	G	G	G	G	G	G	G
Xylene	G	P	G	G	G	G	G	G	G
Naphthalene	G								

CODE

- G = Good, no effect
 F = Fair, swells, softens, slow solvent action.
 P = Poor, not recommended. Destroys filter porosity.
 D = Dissolves completely.
 ** = Trade Mark, E.I. DuPont.
 *** = Trade Mark, Dow Chemical Co.
 + = Trade Mark, Allied Chemical Co.
 * = The words Cellosolve, Metricel and
 Acropor are Registered Trade Marks.

NOTES

1. The Gelman membranes are made by the Gelman Instrument Co. Ann Arbor, Michigan, U.S.A.
 2. Triacetate = cellulose triacetate. Vinyl metricel type VM is a polyvinyl chloride. Fluoride metricel, type VF is polyvinylidene fluoride.
- Alpha metricel is a regenerated (from rayon) cellulose acropor type and is an acrylonitrile - polyvinylchloride copolymer reinforced with nylon.

filling although with practice this step is not essential).

The whole operation was done as quickly as possible (~ 1–2 min) to minimize the time that the membrane surface was exposed to the atmosphere.

ii) *Location*. The accumulator was then placed, membrane upwards, in a plastic bucket of distilled water and transported to the test site. The accumulators were removed from the buckets and located in the concrete blocks. An alternative method was not to use the plastic buckets but to keep the membrane surface wet by the intermittent application of distilled, deionised water from a laboratory wash bottle. The space between the accumulator and the concrete wall was packed with $\frac{1}{2}$ " thick polyurethane foam to provide a firm fit. The plastics coated wire cages were then placed over the concrete blocks and secured with wire ties. The complete assembly was then placed at the chosen site in the river. The site (e.g. river bed) was chosen so that the entire assembly was at least 6 inches below the surface of the water when the water was at its normal lowest level, and the river bed was sufficiently soft to accept holding stakes for the accumulators. The membranes were inclined at about 20° to the flow of water.

Modification to the method of fixing was made when the accumulators were placed in a sewage works outfall or in a sewage treatment plant settling tank.

The accumulators were inspected regularly during the trial period. During the trial, the assembly was removed from the water and any levers or other debris were detached from the cage. The cage was removed from the block and the accumulator and membrane rinsed rapidly with distilled, deionised water to remove any dirt or small particles. Normally, the membrane was very clean. Aliquots of the organic solvent were removed for analysis and a known amount of fresh solvent was added to maintain the original volume. At the conclusion of the trial, the whole sample was kept for analysis.

Theoretical considerations

a) *Accumulation process*

Accumulation of organic compounds in the organic solvent occurs only if the organic compound is soluble in the organic solvent. Thus, the extent of accumulation will depend upon the solubility of the organic compound in the organic solvent and will be governed by the partition coefficient. The process of accumulation therefore is one of solvent extraction. The main difference from normal solvent extraction procedures is that the two essentially immiscible solvents are separated by a membrane, which permits organic molecules to pass from the aqueous phase into the organic phase, but which prevents significant transfer into the organic phase and vice-versa. Another difference from normal solvent

extraction procedures is that whereas agitation of the aqueous phase may occur (either in the laboratory equipment by the gas stirrer (figure 1) or by virtue of the flow of water over the membrane in a river or sewage works outfall), the organic phase in the design of accumulator is unstirred.

Movement of water on the membrane surface will minimize boundary layer effects; and rapid movement will increase the rate of transfer of organic compounds across the water-solvent interface.

Lack of agitation in the organic phase will, therefore, minimise the 'back-diffusion' of accumulated organic materials which would occur when an equilibrium situation was disturbed as a result of a decrease in the equilibrium solute concentration in the aqueous phase. Thus in the practical situation, e.g. a flowing river, where the concentration of organic compound in the river may vary during the accumulation period, it is theoretically possible for the accumulator to contain more organic compound than would be forecast from a knowledge of the partition coefficient and the average concentration of organic compound in the water during the test period (i.e. a true equilibrium system might never be achieved).

b) *Surface properties of polymer membranes*

In the case of two different membranes, for example one made from Cellophane (regenerated cellulose) and the other from polytetrafluoroethylene, (PTFE), the polymers have different surface properties (surface energies). Cellophane is hydrophilic and therefore more easily wetted by water than by carbon tetrachloride. PTFE is hydrophobic and more easily wetted by carbon tetrachloride than by water. These properties are likely to determine the location of the aqueous-organic liquid interface in the proposed accumulator systems which, in turn, may affect the rate of transfer of organic compounds across the membrane. The two systems may be represented as shown in Figure 4 of the accompanying drawings. Thus, for a hydrophobic membrane the aqueous-organic liquid interface is nearer to the aqueous compartment of the accumulator; the opposite is true for the hydrophilic membrane. Consider the transfer of an organic molecule through the pores of the hydrophilic and hydrophobic membranes. Since the rate of stirring of the aqueous phase is unlikely to affect diffusion through stationary liquid in the pores and if it is assumed that the kinetics of transfer across the water-solvent interface are similar in both systems then it can be seen that transfer through a hydrophobic membrane should be faster than through a hydrophilic one; such differences are likely to be slight. However, other properties may determine the choice of membrane, e.g. organic solvent may be lost more easily through a hydrophobic membrane due to the greater proximity of the

water-organic interface to the exterior of the device.	experiment been continued the indication was that accumulation of these compounds would have continued assuming, of course, that the compounds (which are essentially non-biodegradable) were still present in the water.	70
c) <i>Organic solvent</i>		
The properties of the organic solvent are of major importance. It should exhibit high affinity for the organic molecules under investigation, thereby preventing the accumulator from becoming saturated with accumulated organic molecules during its life-time. Carbon tetrachloride and hexane were preferred for initial studies because of their higher solubility for many organic pollutants of current interest and because of their low solubilities in water. The solubilities of carbon tetrachloride and hexane in water at 20°C are about 0.77 g/l and 0.14 g/l, respectively.	Further evidence of the usefulness of the accumulator was provided by comparing the gas-chromatogram of the hexane in the accumulator with that of a hexane 'grab' sample extract of the water in which the accumulator had been immersed (sewage effluent treatment plant) the chromatograms (Figure 7) were similar.	75
Carbon tetrachloride is more dense (1.59 g/cm ³ at 20°C) and hexane is less dense (0.66 g/cm ³ at 20°C) than water or dilute aqueous solution of organic compounds. However, no major problems were experienced due to the leakage of organic solvent through the membrane as a result of differential pressure at the membrane surface.	Evidence of accumulation of other unidentified compounds (thought to be halogenated compounds) was provided from this analysis.	80
It is important that the solubility of the trapped species is high enough to prevent their precipitation during the anticipated life-time of the accumulator.	After 5 weeks the amounts of dieldrin and γ -benzene hexachloride accumulated were 2.1 μ g (i.e. 6.0×10^{-3} ppm in a 360 ml volume accumulator) and 3.0 μ g (8.4×10^{-3} ppm), respectively. Insufficient 'grab' samples of the water were taken to provide a reliable statistical average concentration of dieldrin and γ -benzene hexachloride in the water over the 5 week period, but typical 'grab' samples gave concentrations of 0.03 to 0.13 μ g/l dieldrin and 0.42 to 0.77 μ g/l γ -benzene hexachloride.	85
d) <i>Biochemical stability of the membrane</i>	The above data were obtained in a system in which the movement of water across the membrane surface was relatively slow. It is forecast that increased accumulation would have been found if a faster flow across the membrane had occurred.	90
It is necessary that the membrane exhibits good biochemical stability in the test environment. It was observed that membranes (regenerated cellulose) showed distinct evidence of biodegradation when they were immersed alone in a river or sewage works outfall for periods of between 3 and 6 weeks. However, none of the accumulator membranes showed evidence of biodegradation after eight weeks' immersion in such test sites. This biochemical stability is probably due to the anti-bacterial action of the organic solvent which occurs at the water-solvent interface in the membrane.	In another experiment in a fast-flowing outflow from a different sewage treatment plant, 1.5 μ g dieldrin and 4.7 μ g γ -benzene hexachloride were accumulated. These materials were not detected in a single 'grab' sample of water.	95
<i>EXAMPLES</i>	All the above data were obtained with accumulators fitted with membranes of area approximately 44 cm ² . Greater accumulation could have occurred with membranes of greater area.	100
The following examples demonstrate the potential of the device.	The results of this experiments show that the device will operate in the expected manner in a practical situation.	105
Table II shows data on the accumulation from dilute aqueous solutions of m-xylene, cresol, dichloromethane and 2-bromopropane by carbon tetrachloride and from dilute aqueous solutions of dieldrin by hexane.	The uses and potential advantages of the device are as follows:	110
Figure 5 shows the results of the experiment with 2-bromopropane graphically; the behaviour is similar to that observed with the other compounds. These data demonstrate the technical feasibility of the device.	i) It will concentrate pollutants present at or below levels near the limits of reliable detection — and therefore aid pollutant identification and/or provide useful information on pollutant background levels.	115
Figure 6 shows the results of a field experiment in which an accumulator filled with hexane was circulated slowly in a secondary sedimentation tank of a sewage effluent treatment plant. Aliquots of the hexane were analysed periodically. The amounts of dieldrin and γ -benzene hexachloride in the hexane increased with time. The experiment was stopped after 5 weeks and the membrane was found to be in good condition. Had the	ii) The amount of pollutant accumulated may, in some circumstances, be mathematically related to the average pollutant concentration in the aqueous system; and the device should be sensitive to short-term surges in pollutant concentration.	120
	iii) Selective accumulation of soluble organic compounds is possible by varying the solvent or using mixed solvents	125
		130

TABLE II
LABORATORY ACCUMULATION EXPERIMENTS

Exp. No.	Organic compound	Initial concentration in aqueous phase, ppm	Accumulating solvent	Concentration of accumulated organic compound ppm at sampling time (hours)
1	m-xylene	100(v/v)	carbon tetrachloride	0(0), 20(2), 24(4), 44(7), 70(24), 68(32), 78(97)
2	o-creosol	120(v/v)	carbon tetrachloride	0(0), 12(2), 16(4), 24(7), 76(24), 92(97)
3	dichloromethane	62(v/v)	carbon tetrachloride	0(0), 30(3), 53(5), 60(21)
4	2-bromo-propane	62(v/v)	carbon tetrachloride	0(0), 24(3), 41(5), 56(21), 56(93),
5	dieleldrin	0.4(w/v)	hexane	0(0), 0.04(2), 0.06(4), 0.08(6), 0.30(23), 0.38(31), 0.42(48), 0.43(119)
6	dieleldrin	0.004(w/v)	hexane	0(0), 0.4(2), 0.7(4), 1.05(7), 1.25(23), 1.60(31), 2.05(39), 2.3(111)
7	dieleldrin	0.0014(w/v)	hexane	0(0), 0.6(3), 2.6(22), 2.8(24), 2.8(28), 3.6(45), 4.0(48), 7.6(213)

In experiments 1-6, the volumes of hexane and aqueous phase were approximately the same.
In experiments 6 and 7, the concentrations of accumulated dieleldrin should be multiplied by 10^{-3}

	iv) Analysis of pollutants is simplified. Very large volumes of water do not have to be processed by time-consuming methods. Direct analysis of accumulated pollutants can be carried out thus minimizing loss of volatile or thermally labile compounds, e.g. solution from the accumulator can be transferred directly to a gas chromatograph or high performance liquid chromatograph. Further concentration of accumulated pollutants, especially those of low volatility, can be achieved by evaporating the solvent. Interference from water-soluble inorganic species is obviated.	pollutants include pesticides, herbicides, lipids, chlorinated and brominated aliphatic hydrocarbons, and poorly-biodegradable industrial chemicals (e.g. nitro aromatics, aromatic ethers, tertiary-butyl substituted phenols, phthalic acid esters, lubricating oil additives).	70
5		In particular, if used in properly conducted monitoring programmes, the device will	
10	v) It is a simple, inexpensive and expendable device. It does not require electrical or other fuel power for its operation. Loss in the field through accident or vandalism would not be a major financial consideration. This together with the advantages stated in (iv), could allow organisations with limited financial resources and analytical equipment of modest sensitivity to obtain useful information.	i) overcome many of the problems associated with conventional sampling and analytical procedures, e.g. it is costly and tedious to take the very large numbers of 'grab' samples necessary for statistical purposes and to process large volumes of particle-containing water	75
15		ii) provide a better early warning that pollutant levels were rising, or approaching or had reached dangerous levels; or assurance that control methods were satisfactory	80
20		iii) more easily identify sites suitable for research investigation; and conversely, identify sites which require little investigation.	85
25	In considering the potential of the accumulator other methods of accumulating organic compounds should be considered in particular adsorption onto charcoal and ion exchange resins. Whilst it is not suggested that the IRI accumulator would be a complete substitute for either of these methods it is suggested that it has several advantages compared to 'adsorption' processes which could make it, if used wither alone or in conjunction with other methods, a valuable tool in environmental monitoring.	Particular applications include	
30		a) identifying and quantifying pollutants in chlorinated drinking water, waste waters from synthetic monomer plastic-manufacturing and industrial chemical plants	90
35		b) plotting pollutant contour maps in estuarial waters or effluent outflows; determining the effectiveness of sequential unit process treatments in effluent plant	95
40	Problems associated with 'adsorption' systems, some of which are not found with the present invention, include	c) concentrating organic compounds in drinking water for toxicity testing	
45	i) non-selective adsorption (e.g. it is reported that over 100 non-biodegradable pollutants were extracted from a Rhine waterworks carbon filter). This could, of course, be advantageous in some circumstances	d) investigating composition of radioactive materials in waste waters.	100
50	ii) preferential adsorption and blocking of adsorption sites by pollutants or compounds of little interest, present in excess	CONCLUSIONS	
55	iii) contamination of system and/or blocking of adsorption sites by silt, weed, etc.	Our laboratory experiments have shown that the device can be used to accumulate organic materials from aqueous solution. Our field experiments have shown that the device can be used successfully in practical situations where a knowledge of the type and amounts of organic pollutants is required.	105
60	iv) Adsorption of non-soluble pollutants (it is usually desirable to distinguish between dissolved and undissolved pollutants)	The method and apparatus of the invention are not restricted to the use of a regenerated cellulose membrane and hexane or carbon tetrachloride as the solvent. The material from which the body of the accumulator device is made should not contain organic materials which can be extracted albeit slowly by the organic solvent. A wide range of other solvents with low water solubilities can be used, depending on the organic compounds being investigated, e.g. benzene, toluene, diethyl ether and ethyl acetate. Similarly, other polymeric membranes than those specifically referred to can be used subject to their compatibility with the organic solvent, their ability to allow the required diffusion processes to occur and their resistance to biodegradation.	110
65	v) possible biodegradation of adsorbed species (solvents used in the accumulator of the present invention have been shown to be effective bacteriocides in operation)	The accumulator device can be located for example, on a river bed. However the device need not be immersed directly in the river or effluent stream under test. It is convenient	115
	vi) necessity of extracting adsorbed pollutants from adsorbent (problems with incomplete recovery, use of large volumes of solvent, and loss of volatile and thermally labile materials have been encountered).		120
	The accumulator is applicable to a wide range of organic pollutants which exhibit high solubility in solvents which are sparingly soluble in water. Relevant classes of		125
			130

to locate the device in a bath or other container placed, for example, on the river bank, and to pump the water through the bath or container in a regular fashion.	xylene, toluene, hydrocarbons, chlorinated hydrocarbons and other organic liquids possessing low solubility in water.	65
5 One improvement in the design of the accumulator is to incorporate a stirring device close to the membrane surface. Mechanical stirring in, for example, slow-moving streams minimises the boundary	3. A device according to claim 2, wherein said organic medium is hexane.	
10 layer effects and increases the rate of diffusion of organic compound across the membranes. Such a device results in a more constant rate of accumulation than may be found in the device results in a more constant rate of	4. A device according to claim 2, wherein said organic medium is chloroform or carbon tetrachloride.	70
15 accumulation than may be found in the devices described above. A suitable design is shown in Figures 8 and 9 of the accompanying drawings. A metal housing 24 is provided with an interior lining 25 of glass or other inert material. A membrane 26 is secured to the mouth 27 of the housing 24 as shown below in Figure 9. A motor block 28 is supported above the housing 24 by several connecting rods 29. A motor 37 drives a stirrer blade 30 and is energised by a long-life battery 38 (Figure 10). Figure 9 is a more detailed sectional elevation of the housing 24 which is of stainless steel (the glass or like lining 25 is omitted for clarity). The membrane 26 is held between plastic annuli 31 and 32 respectively.	5. A device according to claim 1, wherein said porous membrane is composed of a material selected from regenerated cellulose, vinyl chloride homopolymers and copolymers, polyvinylidene fluoride, acrylonitrilepolyvinylchloride and polytetrafluoroethylene.	75
20	6. A device according to claim 1, wherein said housing is composed of glass and is filled with hexane, and said membrane is composed of regenerated cellulose wetted by said hexane.	80
25	7. An installation for accumulating organic materials from a water system comprising a device according to claim 6, and further comprising a concrete block provided with an opening for receiving said device and allowing water to flow freely over said device means for supporting said device within said concrete block at the mouth of said opening and means for anchoring said concrete block with said device at a chosen location in a water system.	85
30	8. A method of monitoring the organic materials content in a water system comprising the steps of allowing water from the water system to contact one side of a porous membrane capable of allowing said organic materials to diffuse therethrough, maintaining in contact with the other side of said porous membrane an organic medium (as herein defined) being capable of dissolving said organic materials and removing at intervals samples of said organic medium containing said organic materials and analysing said samples to determine the accumulation of said organic materials over a predetermined period.	90
35	9. A device for accumulating organic materials from a water system substantially as herein described with reference to Figures 1, 2 and 8 of the accompanying drawings.	95
40	10. An installation for accumulating organic materials from a water system as claimed in Claim 7 substantially as herein described with reference to Figure 3 of the accompanying drawings.	100
45	Elkington and Fife, Chatered Patent Agents, High Holborn House, 52-54 High Holborn, London WC1V 6SH	105
50	Agents for the Applicants	110
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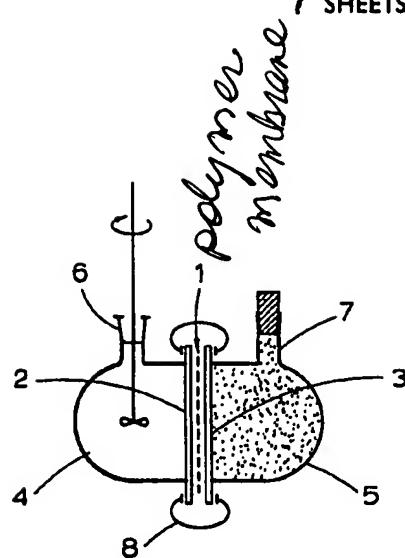


Fig. 1

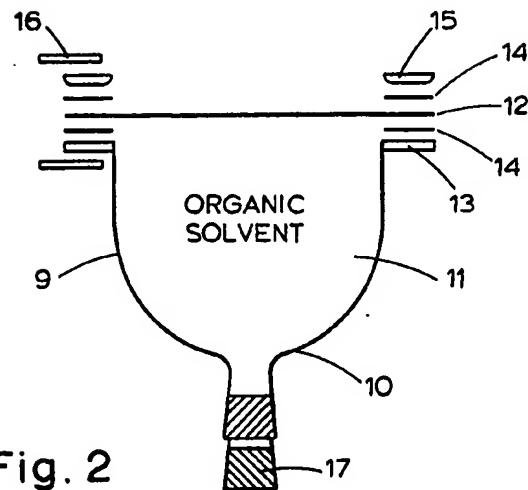


Fig. 2

1566253 COMPLETE SPECIFICATION

7 SHEETS *This drawing is a reproduction of
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Sheet 2*

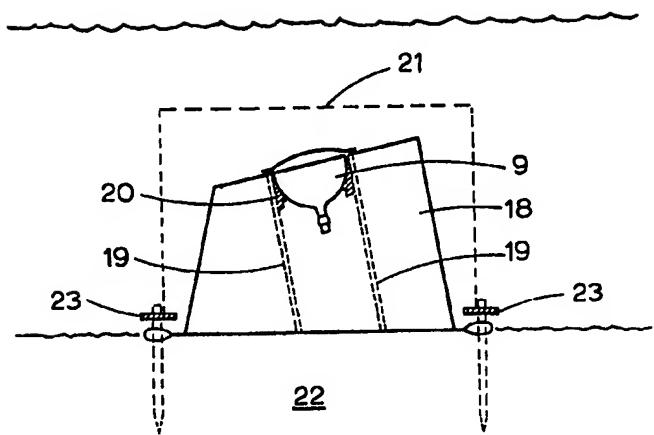
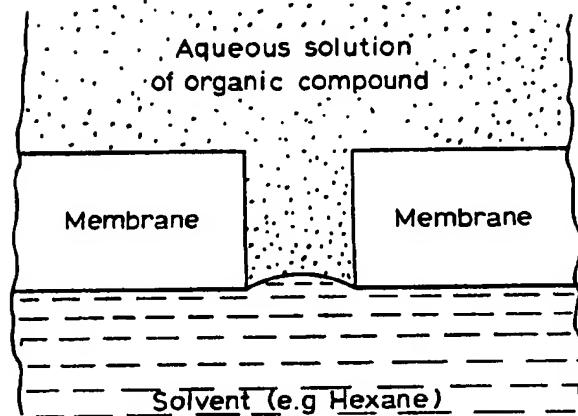


Fig. 3

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Sheet 3*

Pore in hydrophilic membrane.



Pore in hydrophobic membrane.

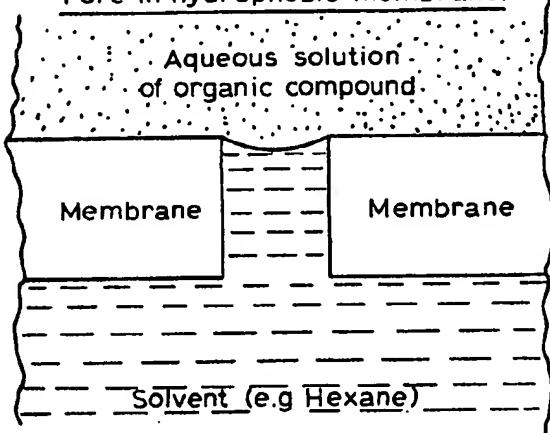


Fig. 4

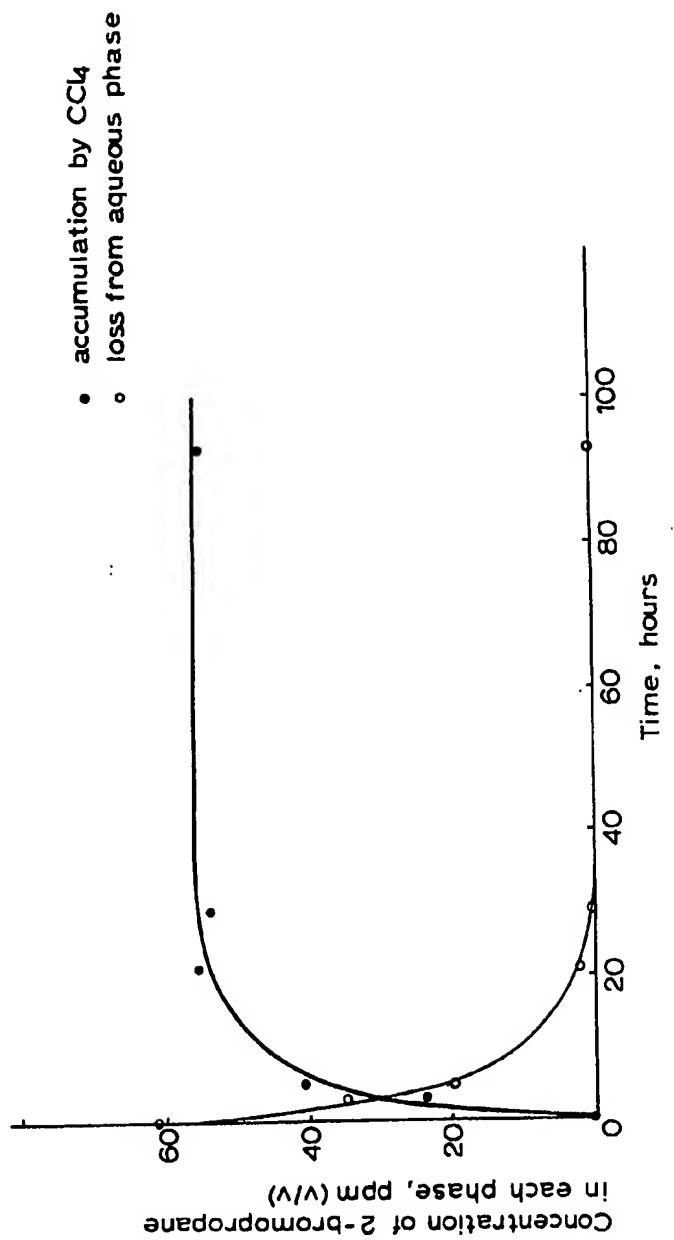


Fig. 5

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Sheet 5*

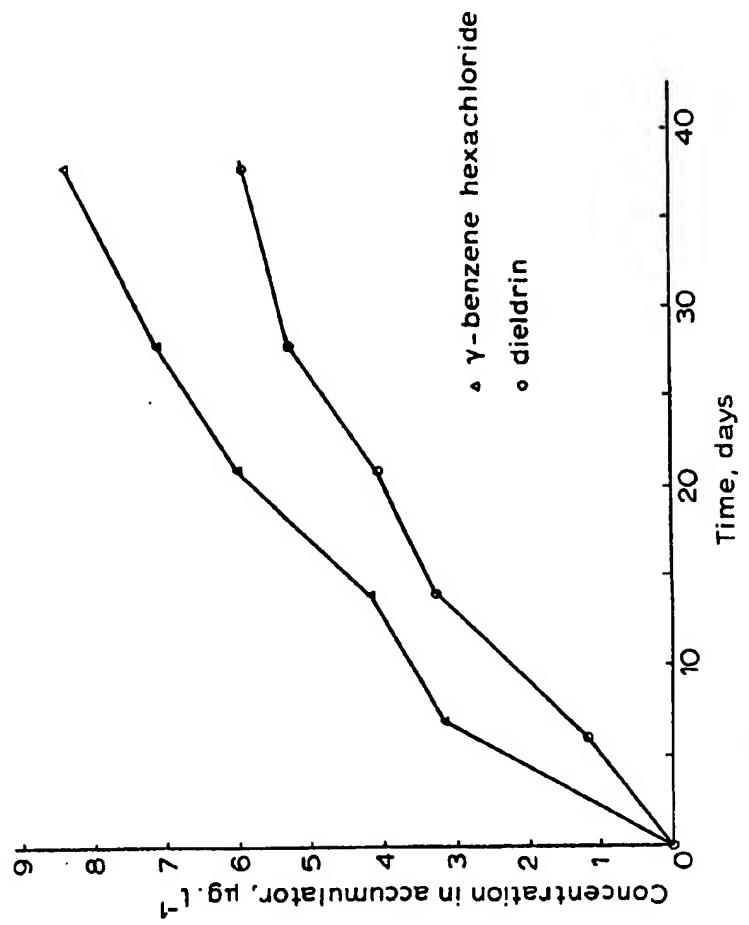


Fig. 6

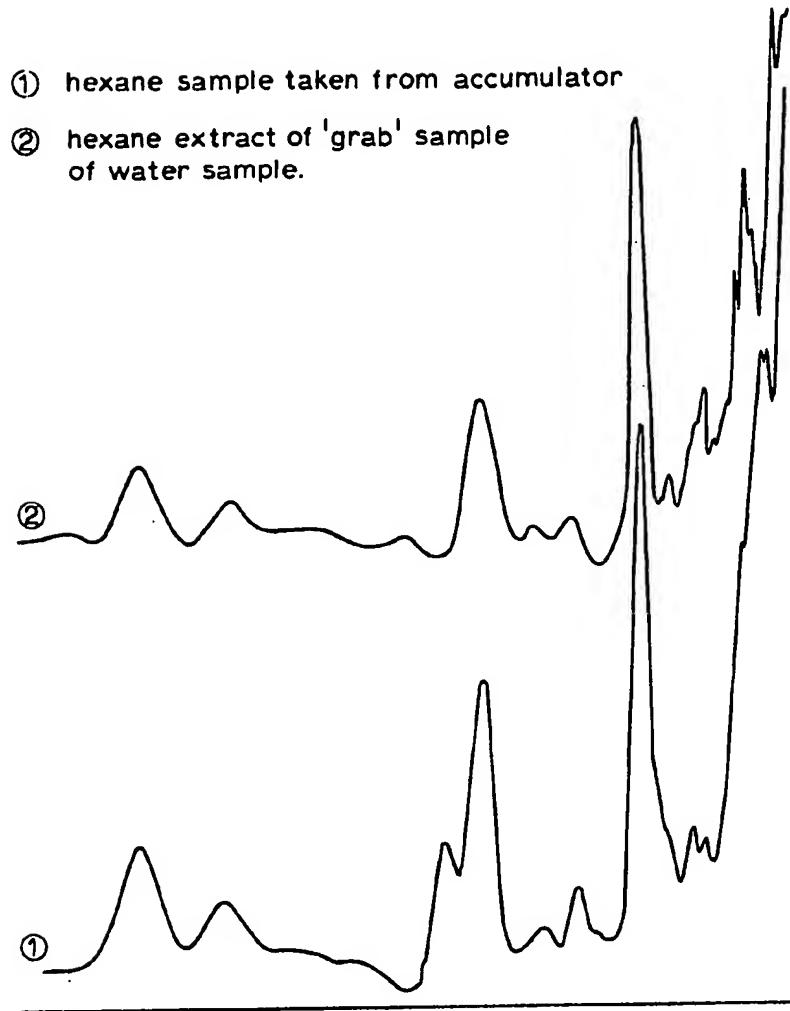


Fig. 7

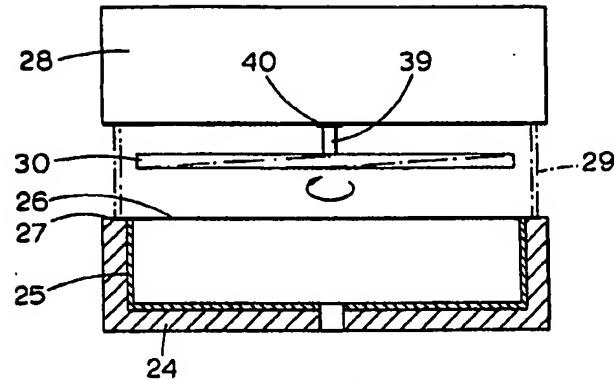


Fig.8

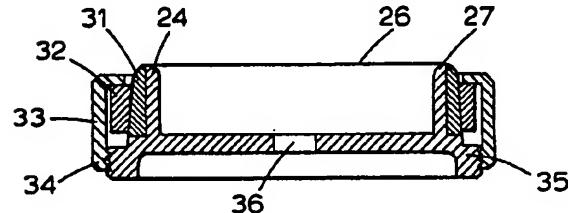


Fig. 9

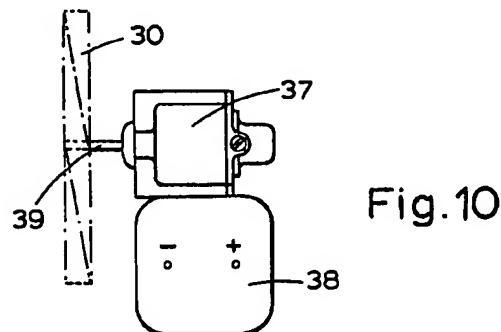


Fig. 10